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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: HITACHI CHEMICAL CO., LTD.

SANYO ELECTRIC CO., LTD.

Application No.: 10/570,349   Group Art Unit: 1795

Filing Date: 03/03/2006   Examiner: THOMAS, BRENT C

Title: NONAQUEOUS ELECTROLYTE SECONDARY BATTERY NEGATIVE ELECTRODE MATERIAL, MANUFACTURING METHOD THEREOF, NONAQUEOUS ELECTROLYTE SECONDARY BATTERY NEGATIVE ELECTRODE WITH THE NEGATIVE ELECTRODE MATERIAL AND NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

DECLARATION UNDER 37 CFR 1.132

Assistant Commissioner for Patents

Washington D.C. 20231

Dear Sir:

I, Kiyoshi SUZUKI, a citizen of Japan, one of the inventors of the above-identified application, hereby declare and state that:

1.   I received a bachelor's degree of industrial chemistry in 1998 from the department of science and engineering, Tokyo University of Science, and a master's degree of industrial chemistry in 2000 from the faculty of industrial chemistry, Tokyo University of Science.

2.   I have been employed by Hitachi Chemical Co. Ltd. as a researcher since 2000.

3.   I am engaged mainly in research in the field of chemical

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battery.

I understand the above application has been rejected over EP 0917228 A1 and JP2000-203818. In order to show the effects of the present invention, the following experiments were undertaken under my direction.

1. Purpose:

The purpose of this study was to verify that the present invention has a superior effect than that of the invention described in cited reference since "superficial carbonization rate" is the range between 0.001 and 0.01.

2. Experiments A and B

This experiment was performed just like the Examples described in the specification of the present application, as follows.

(A) Preparation of Raw Material Graphite Particles

One hundred parts by mass of cokes powder having an average particle diameter of 5 μm, 40 parts by mass of tar pitch, 25 parts by mass of silicon carbide having an average particle diameter of 48 μm and 20 parts by mass of coal tar were mixed, followed by further mixing at 270°C for 1 hr. An obtained mixture was pulverized, followed by molding under pressure into pellets, further followed by firing in nitrogen at 900°C, still further followed by graphitizing at 3000°C by use of an Acheson furnace, followed by pulverizing by use

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of a hammer mill, further followed by sieving with a 200 mesh standard sieve, and thereby graphite particles were prepared. According to a scanning electron microscope (SEM) photograph of the obtained graphite particles, the graphite particles were found to have a structure where a plurality of flat particles assembled or bonded with each other non-parallel in alignment surface. Physicality values of the obtained graphite particles are shown in Table 1. Measurement methods of the respective physicality values are as follows.

(1) Average particle diameter: A particle diameter at 50%D with Laser diffraction particle distribution analyzer (SALD-3000, manufactured by Shimadzu Corp.) was taken as an average particle diameter.

(2) Aspect ratio: Major axes and minor axes of 100 particles arbitrarily extracted from a SEM photograph of the graphite particles were measured, ratios thereof were obtained according to an equation below, and an average value thereof was taken as the aspect ratio.

Aspect ratio = major axis/minor axis

(3) True specific gravity: Measured according to a butanol replacement method.

(4) Bulk density: A sample of graphite particles was poured into a 200 ml glass measuring cylinder and tapped until a

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sample volume did not show further change, followed by measuring the sample volume. The bulk density was obtained by dividing a sample weight by the obtained sample volume.

(5) Interplanar spacing (d002): The interplanar spacing was measured by use of a wide angle X-ray diffractometer (manufactured by Phillips) with Cu-Kα line monochromatized by use of a monochrometer and with high purity silicon as a reference material.

(6) Specific surface area: A nitrogen absorption at liquid nitrogen temperature was measured according to a multipoint method with ASAP 2010 (manufactured by Maicromeritics), and the specific surface area was calculated according to the BET method.

(7) Pore volume: By use of Autoscan 33 (manufactured by Yuasa Ionics Inc.), a pore volume in the range of 10 to 10^5 nm was measured.

(8) Peak intensity ratio in Raman spectrum: By use of NRS-2100 (manufactured by JASCO Corporation), a measurement was carried out under the conditions of laser output: 10 mW, spectrometer: F single, incident slit width: 800 μm, times of integration: two times, and exposure time: 120 sec.

(9) Slurry viscosity: Slurry with a composition below was

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prepared by use of a mortar, followed by measuring the viscosity by use of a MODEL DV-III manufactured by Brookfield at the shearing speed of 4 sec^{-1} and 25°C.

Slurry composition

Polyvinylidene fluoride/(polyvinylidene fluoride + graphite particles) = 0.1 (by weight ratio)

Solvent: N-methyl-2-pyrollidone

Total solid concentration (graphite particles, polyvinylidene fluoride) in paste = 45%

Polyvinylidene fluoride: #1120, manufactured by Kureha Chemical Industry Co., Ltd.

Each of solutions obtained by dissolving 18g (Experiment A), 24g (Experiment B) of coal tar pitch (softening point: 98°C and carbonization rate: 50%), respectively, in tetrahydrofuran to be 900 g was poured into a flask provided with a condenser, and thereto 600 g of graphite particles shown in Table 1 was added. The solution was heated to a boiling point under agitation in a water bath, followed by mixing for 1 hr. In the next place, the solution containing the graphite particles was transferred to a rotary evaporator, followed by removing tetrahydrofuran, further followed by drying at 100°C for 1 hr by use of a vacuum dryer, and thereby graphite particles covered with coal tar pitch were obtained. The obtained graphite particles covered with coal tar pitch were heated to 1300°C at a temperature rise rate of 20°C/h under nitrogen stream, held there for 1 hr, and thereby

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graphite particles covered with carbon were obtained. The obtained graphite particles covered with carbon were pulverized by use of a cutter mill followed by passing through a 250 mesh standard sieve, and thereby a sample of negative electrode material was obtained. When the coal tar pitch was singularly heated to 1300°C at a temperature rise rate of 20°C/hr under nitrogen stream followed by holding there for 1 hr, the carbonization rate was 49%. From the above value and amounts of coated coal tar pitch, superficial carbon ratios of the respective examples were calculated and found to be 0.015 (Experiment A), 0.02 (Experiment B) respectively. Characteristics of obtained samples of negative electrode materials of the respective examples are shown in Table 1.

(B) For the respective samples of negative electrode materials according to Experiments A and B, under the conditions shown in Table 2, evaluations as the lithium ion secondary battery negative electrode were carried out. Results are shown in Table 1. In Table 1, the data of example 1 to 4 and comparative example 1 to 3 are shown for the reference.

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[Table 1]

Item	Comparative Example 1	Comparative Example 3	Example 4	Example 3	Example 2	Example 1	Experiment 1	Experiment 2	Comparative Example 2
Superficial carbon rate	0	0.0005	0.001	0.003	0.005	0.01	0.015	0.02	0.03
Average particle diameter (μm)	20.3	20.3	20.8	21.0	21.0	21.3	21.4	21.4	21.5
Aspect ratio	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
True specific gravity	2.24	2.24	2.24	2.24	2.24	2.24	2.24	2.24	2.22
Bulk density (kg/m^3)	750	770	810	840	860	880	890	900	910
Specific surface area (m^2/g)	3.5	3.3	3.1	2.9	2.8	2.7	2.7	2.6	2.5
R value	0.09	0.11	0.12	0.14	0.15	0.17	0.21	0.22	0.24
Slurry viscosity (Pa × s)	3.56	3.40	2.91	2.20	1.83	1.20	1.06	0.88	0.70
Bulk density under 33 MPa (kg/m^3)	1990	1990	1980	1960	1940	1920	1910	1900	1890
Bulk density variation rate when pressure is released	0.154	0.165	0.195	0.212	0.216	0.260	0.308	0.326	0.363
Discharging capacity (Ah/kg)	363	360	361	362	360	361	362	360	358
Charge/discharge efficiency (%)	91.0	91.0	91.0	91.1	90.8	90.9	90.6	90.6	90.5
Charge load characteristics (%)	28	30	32	40	41	41	41	42	42

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[Table 2]

Item		Condition
Cell		Two electrodes (opposite electrode: lithium metal)
Sample weight		8 mg
Electrode area		2.5 cm^2
Binder		Polyvinylidene fluoride (#1120, manufactured by Kureha Chemical Industry Co., Ltd.) 10% by weight
Solvent for preparing electrode material slurry		N-methyl-2-pyrrolidone
Drying condition		110°C, 5 hr, in air
Electrolytic solution		1M LiPF$_6$, ethylene carbonate/methylethyl carbonate (1/1)
Measurement of charge/discharge capacity and charge/discharge efficiency	Charging condition	Constant current charge: 0.2 mA Constant voltage charge: 0V (Li/Li$^+$), cut current 0.02 mA
	Discharging condition	Current: 0.2 mA Cut voltage: 1.5 V (Li/Li$^+$)
Measurement of charge load characteristics		Measurement method 1) Two cycles of charge/discharge under charge/discharge capacity measurement conditions 2) Constant current charge: 0.2 mA, 0V (Li/Li+) cut, discharge: 0.2 mA, 1.5 V (Li/Li+) cut 3) Constant current charge: 1.5 mA, 0 V (Li/Li+) cut, discharge: 0.2 mA, 1.5 V (Li/Li+) cut Charge load characteristics (%) = {constant current (1.5 mA) charge capacity/ constant current (0.2 mA) charge capacity} × 100.

3. Results

As obvious from Table 1, it is found that the Experiments A and B are excellent in "the charge load characteristics" but are not excellent in "the Bulk density variation rate when pressure is released". This result shows that "superficial carbonization rate" must be the range between 0.001 and 0.01 to obtain an excellent effect not only in "the charge load characteristics" but also in "the Bulk density variation rate when pressure is released".

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I hereby declare that all statements made herein of my own knowledge are true and all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of application or any patent issuing thereon.

Date: *Oct 28, 2010*

Kiyoshi Suzuki

Kiyoshi SUZUKI

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